COPY

Consumer and Corporate Affairs Canada | Consommation et Corporations Canada

(11) (A) No. 1 236 642

(45) ISSUED 880510

(52) CLASS 402-344

(51) INT. CL.^{4} C08G 75/02

(19) (CA) CANADIAN PATENT (12)

(54) Process for Production of High to Ultra-High Molecular Weight Linear Polyarylenesulfides

(72) Iizuka, Yo;
Iwasaki, Takao;
Katto, Takayuki;
Shiiki, Zenya,
Japan

(73) Granted to Kureha Kagaku Kogyo Kabushiki Kaisha
Japan

(21) APPLICATION No. 484,413

(22) FILED 850619

(30) PRIORITY DATE Japan (126725/1984) 840620
Japan (188533/1984) 840908

No. OF CLAIMS 29 - NO DRAWING

Canada

PROCESS FOR PRODUCTION OF HIGH TO ULTRA-HIGH MOLECULAR WEIGHT LINEAR POLYARYLENESULFIDES

BACKGROUND OF THE INVENTION

This invention relates to a process for producing a polyarylene sulfide (hereinafter abbreviated as PAS), and more particularly to a novel process for producing a high to ultra-high molecular weight linear PAS at low cost without use of a crosslinking agent or an organic acid salt in its production.

In recent years, highly heat-resistant thermoplastics are increasingly demanded for parts such as those for electrical instruments and motor vehicles.

PAS has properties which can meet such demands. However, it is difficult to obtain this PAS as represented by polyphenylenesulfide of an amply high molecular weight. Consequently, this situation gives rise to the problem of extreme difficulty in obtaining particularly fibers and films for which high strength is required or molded articles for which high impact strength is required.

The present invention provides a process for producing inexpensively a markedly high molecular weight linear PAS in order to overcome these problems.

Prior art

As a typical process for production of PAS, Japanese Patent Publication No. 3368/1970 discloses a process in which a dihalo-aromatic compound is reacted with sodium sulfide in an organic amide solvent such as N-methylpyrrolidone. However, the PAS produced by this process has low molecular weight and melt viscosity, and it is difficult to fabricate it into a film, sheet or fiber.

Under such a state of the art, various proposals have been made to improve the process as mentioned above in order to obtain PAS with higher polymerization degree. In the most typical process as disclosed

in Japanese Patent Publication No. 12240/1977, an alkali metal carboxylate is employed as the polymerization aid in the above reaction system. According to this process, it is necessary to use the polymerization aid in an amount substantially equimolar to the alkali metal sulfide. Further, for obtaining PAS with higher polymerization degree, an expensive lithium or sodium benzoate among various polymerization aids is required for use in a large amount. This requirement results in increased production cost of PAS, resulting in commercial disadvantage. Also, according to this process, a large amount of organic acid may be entrained in the disposed waste water during recovery of PAS after polymerization reaction, whereby problems in pollution may be caused. For prevention of such problems, enormous costs are undoubtedly necessary, thus involving serious problems from the economical point of view.

In another proposed process for obtaining PAS with high polymerization degree, a trivalent or higher polyhalo-aromatic compound is used as a crosslinking agent or a branching agent, or a polymer is subjected to high temperature treatment in the presence of oxygen (reference: Japanese Laid-Open Patent Publication No. 136100/1978, etc.). According to this process, it is possible to obtain easily a high molecular weight PAS having an apparent melt viscosity of some tens of thousands poise. However, since this PAS is a polymer crosslinked or branched to a high degree, it has poor fiber-forming property, and it is difficult to mold it into films or fibers. Also, even if molded articles could be obtained, there is still the problem of their being mechanically extremely fragile because their molecular chains are basically short.

SUMMARY OF THE INVENTION

In view of the above circumstances, we have made investigations in detail on the polymerization mechanism

in a simple polymerization system of an alkali metal sulfide and a dihalo-aromatic compound, in order to develop a process for producing a PAS which has high melt viscosity and yet is linear at low cost without use of a polymerization aid such as alkali metal carboxylates. As a result, it has now been found, suprisingly, that a linear PAS of a markedly high molecular weight with a melt viscosity of about some thousands to some tens of thousands poise can be readily produced without the use of an aid by forming a PAS prepolymer of low to medium molecular weight according to a preliminary polymerization, then elevating the temperature by heating the polymerization system under strongly alkaline conditions with addition of a phase separating agent to the polymerization system, thereby separating the system into two liquid phases of high viscosity phase (polymer solution phase) and low viscosity phase (solvent phase), and carrying out the reaction under such a state.

According to one aspect of the present invention there is provided a process for producing a high to ultra-high molecular weight linear polyarylene sulfide which comprises subjecting an arylene sulfide prepolymer, having a melt viscosity of 5 to 3000 poise measured at 310 C and a shear rate of 200 sec^{-1}, to a liquid-liquid two-phase separated polymerization under strongly alkaline conditions

at a temperature of about 245 to 290°C.

According to a further aspect of the present invention there is provided a process for producing a high to ultra-high molecular weight linear polyarylene sulfide which comprises forming an arylene sulfid repolymer and further polymerizing said prepolymer under strongly alkaline conditions at a temperature of about 245°C to 290°C in a liquid-liquid two-phase separated polymerization.

Thus according to another aspect the process for producing the high molecular weight to ultra-high molecular weight linear polyarylenesulfide according to the present invention comprises carrying out a two-phase separated polymerization comprising dissolving an arylenesulfide prepolymer having a melt viscosity of 5 to 3,000 poise (at 310°C, shearing rate = 200 $(sec)^{-1}$) in a poor solvent under a strongly alkaline condition (in a pH range of from 9.5 to 14 of the reaction mixture when diluted 10-fold with water) in a temperature range of from 245°C to 290°C into a liquid-liquid two-phase separated state and maintaining this state for 1 to 50 hours to convert the arylenesulfide prepolymer into a high molecular weight polymer, then separating the polymer from the polymerization system and purifying the polymer after neutralization.

The term "non-good solvent" or "poor solvent" herein used means such a poor solvent that a polyarylene-sulfide having a melt viscosity of 5 to 3,000 poise (measured at 310°C and a shearina rate = 200 $(sec)^{-1}$) forms a liquid-

liquid two phase separated state at a temperature of from 245°C to 290°C.

The polymerization mechanism of the present invention has not yet completely been clarified, but the

main mechanism may be hypothesized to be a synergetic mechanism of "condensation polymerization" and "phase separation". Regardless of the true nature of the mechanism, it may certainly be considered that the separating action between the two liquid-liquid phases is an important point. To explain schematically the polymerization mechanism, the main mechanism may be considered to consist of a condensation polymerization mechanism in which the polymer terminal groups participate in the reaction as shown below in the reaction scheme (1) and the eliminating separating action of the MX (salt) which is the reaction product through migration to the solvent phase during phase separation into two liquid-liquid phases of the polymer solution phase and the solvent phase, or alternatively the contact preventing action between harmful substances (presumably organic sulfur compounds, etc.) which may promote decomposition of the polymer chains and the polymer formed, as well as the fractionating action of low molecular weight oligomers which have migrated into the above solvent phase.

(1) $\sim\sim ArX + MS\text{-}Ar\sim\sim \rightarrow \sim\sim Ar\text{-}S\text{-}Ar\sim\sim + MX$
(Ar: arylene group, M: alkali metal atom, X: halogen atom, MX: alkali metal salt).

Although it has not been ascertained so far whether the above mechanism is the main one, a prepolymer can be allowed to react under strongly alkaline, high temperature and liquid-liquid two-phase separation conditions to be changed to a high molecular weight or ultra-high molecular weight polymer, regardless of the mechanism involved. Accordingly, this reaction is described tentatively as "two-phase separated polymerization".

In contrast, polymerization conducted in an organic amide solvent with small water content conventionally practiced in the prior art, in which the polymer formed is dissolved substantially homogeneously at a higher temperature (above about 235°C) with forming substantially one liquid phase and also the polymer formed is practically

precipitated from the system at a lower temperature (below about 235°C) with forming substantially one liquid phase. Such polymerization is described as "preliminary polymerization" hereinafter.

For carrying out the two-phase separated polymerization of the present invention, a prepolymer to form the polymer phase is required, but it is difficult to subject materials of an alkali metal sulfide and a dihalo-aromatic hydrocarbon directly to the two-phase separated polymerization. On the other hand, preliminary polmerization of the starting materials of an alkali metal sulfide and a dihalo-aromatic hydrocarbon in an organic amide with a low water content can be readily carried out to form a low to medium molecular weight polyarylensulfide.

Therefore, for obtaining a high to ultra-high molecular weight polyarylenesulfide, it is desirable to carry out continuously the preliminary polymerization and the two-phase separated polymerization. The present invention is practiced by such a continuous process.

Further, for obtaining particularly an ultra high molecular weight PAS with a melt viscosity of 7,000 poise or higher, it is effective to employ the process in which a low to medium molecular weight arylenesulfide prepolymer formed by the preliminary polymerization is separated once from the polymerization system and cleaned before it is returned again to the polymerization system for carrying out the liquid-liquid two-phase separated polymerization. This procedure for obtaining the ultra-high molecular weight PAS is also

one of the techniques of the present invention.

According to the process of the present invention, even an ultra-high molecular weight linear PAS with a melt viscosity of 10,000 poise or higher can easily be produced without the aid of a crosslinking agent or an expensive polymerization aid (e.g., carboxylates). Since no crosslinking agent is employed, the PAS

obtained is linear, and filaments or films can easily be formed therefrom. Also, molded articles from this polymer possess excellent mechanical properties. The process is also very economically advantageous without the possibility of pollution because no polymerization aid (e.g., organic carboxylates) is employed.

DETAILED DESCRIPTION OF THE INVENTION

The process for production of a high to ultra-high molecular weight PAS according to the present invention comprises, basically, forming PAS molecules through bonding between an alkali metal sulfide and a dihalo-aromatic compound and/or converting the PAS molecules into a high molecular weight polymer.

Starting materials

Alkali metal sulfide

The alkali metal sulfide to be used in the present invention includes lithium sulfide, sodium sulfide, potassium sulfide, rubidium sulfide, cesium sulfide and mixtures thereof. These alkali metal sulfides can be used as hydrates or aqueous mixtures, or in anhydrous forms.

Among these alkali sulfides, sodium sulfide is the least expensive and is commercially preferred.

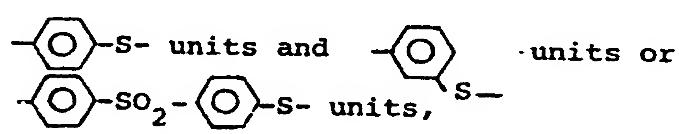
It is also possible to use a small amount of an alkali metal hydroxide in combination in order to neutralize an acidic salt (e.g., alkali metal disulfides and alkali bicarbonates) which may sometimes occur in minute amount in an alkali metal sulfide.

Dihalo-aromatic compound

The dihalo-aromatic compound to be used in the present invention can be, for example, any of dihalo-aromatic compounds as disclosed in Japanese Laid-open Patent Publication No. 22926/1984. Particularly preferred are p-dichlorobenzene, m-dichlorobenzene, 2,5-dichlorotoluene, 2,5-dichloro-p-xylene, p-dibromobenzene, 1,4-dichloronaphthalene, 1-methoxy-2,5-dichlorobenzene, 4,4'-dichlorobiphenyl, 3,5-dichlorobenzoic acid, p,p'-

dichlorodiphenylether, p,p'-dichlorodiphenylsulfone, p,p'-dichlorodiphenylsulfoxide, p,p'-dichlorodiphenylketone, and the like. Among these, those composed mainly of para-dihalobenzene, typically p-dichlorobenzene, are especially preferred.

By appropriate selection and combination of dihalo-aromatic compounds, a random or block copolymer containing two or more different reaction units can be obtained. For example, when employing p-dichlorobenzene in combination with m-dichlorobenzene or p,p'-dichlorodiphenylsulfone, a random or block copolymer containing:



can be obtained. Further, a small amount of a polyhalo-aromatic compound (e.g., trichlorobenzene) within the range which will not impair linearity may also be employed in combination, but no such compound is ordinarily required.

Polymerization solvent

The organic amide solvent to be used in the polymerization step for forming the prepolymer of the present invention (the first step) can be selected from N-methylpyrrolidone (NMP), N-ethyl-pyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide, N-methylcaprolactam, tetramethylurea, hexamethylphosphorotriamide, and mixtures thereof. Among these, N-methylpyrrolidone is particularly preferred from viewpoints such as chemical stability and ability to produce readily a high molecular weight polymer. The organic amide as the polymerization solvent is desirably an aprotic compound.

Also in the polymerization step for forming an ultra-high molecular linear polymer from the prepolymer of the present invention, the above organic amide can

of course be used. Otherwise, it is also possible to employ, for example, aromatic hydrocarbons ($C_6 - C_{30}$), aliphatic hydrocarbons ($C_6 - C_{30}$), ethers ($C_5 - C_{30}$), ketones ($C_5 - C_{30}$), pyridine or quinoline or derivatives of these ($C_5 - C_{30}$), and mixtures thereof as such or as mixtures with organic amides.

Polymerization process

The process for production of the high to ultra-high molecular weight PAS of the present invention is inclusive of the process [A] comprising the steps of preliminary polymerization and two-phase separated polymerization or the process [B] comprising the steps of preliminary polymerization, prepolymer separation (cleaning), and two-phase separated polymerization. The process [A] is an economical process for production of high molecular weight PAS having a melt viscosity up to about 7,000 poise, while the process [B] comprising more steps than the process [A] is suitable for production of an ultra-high molecular weight PAS having a melt viscosity higher than 7,000 poise. The process [A] and the process [B] will now be described in detail.

Process [A]

For preparation of the arylensulfide prepolymer (5 - 3,000 poise) to be used for this process, a simple preliminary polymerization process, in which it is prepared by allowing an alkali metal sulfide to react with a dihalo-substituted aromatic compound in an organic amide solvent, or an improved preliminary polymerization process, in which a prepolymer with a greater molecular weight is prepared by permitting an organic carboxylic acid alkali salt, $Ca(OH)_2$, CaO, etc. to coexist in the reaction system, can be applied. However, in the process [A], since the polymerized slurry formed in the preliminary polymerization is used as such in the

subsequent two-phase separated polymerization, the simple system without the co-presence of any third substance is preferred.

The process [A] is commercially a very economical process in that the preliminary polymerization step and the two-phase separated polymerization step can be readily practiced continuously.

First, the step of forming a low to medium molecular weight prepolymer should desirably be performed by carrying out polymerization in a polymerization reaction system containing 0.5 to 2.4 moles of water per mole of the alkali metal sulfide at a temperature in the range of from 160 to 270°C, particularly from 180 to 235°C, until the conversion of the dihalo-aromatic compound becomes 70 mole % to 98 mole % (or until the residual alkali metal sulfide becomes 30 mole % or less) to form a PAS having a melt viscosity of 5 to 300 poise [in the present invention, the melt viscosity is measured at 310°C at a shearing rate of $200(\text{sec.})^{-1}$].

In practicing the process, first, an alkali metal sulfide and a dihalo-aromatic compound are added into an organic solvent, desirably under an inert gas atmosphere, at a temperature in the range of from room temperature to 130°C, and the temperature is elevated to a desired temperature at which the reaction is carried out. Here, if the water content in the alkali metal sulfide is less than the desired content, the necessary amount of water is added for supplementation. If it is too much, according to the method known to those skilled in the art, that is, under atmospheric pressure while the temperature of the solvent (and the alkali metal sulfide) is raised from 150°C to about 210°C, the unnecessary amount of water is expelled out of the system before addition of the dihalo-aromatic compound.

During this operation, if an excessive amount of

water is removed, the quantity corresponding to shortage is supplemented by addition of water. The amount of the co-existing water in the polymerization system is within the range of from 0.5 mole to 2.4 moles per mole of the alkali metal sulfide charged. Particularly, the range of from 1.0 mol to 2.0 moles will readily afford a high molecular weight PAS as the PAS finally obtained. At a level less than 0.5 mole, undesirable reactions such as decomposition of the PAS formed will occur. On the other hand, at a level in excess of 2.4 moles, decomposition reactions of the solvent or the PAS formed may occur, or the polymerization rate may become markedly smaller. Thus, quantities outside of the above range are not desirable.

The preliminary polymerization is preferably conducted at a temperature in the range of from 160 to 260°C, particularly from 180 to 235°C. At a temperature lower than 160°C, the reaction rate is too slow, while at a temperature over 260°C, the PAS formed is liable to be decomposed to produce only a PAS with extremely low melt viscosity.

The amount of the dihalo-aromatic compound used is desirably within the range of from 0.9 mole to 1.1 moles per mole of the alkali metal sulfide, particularly preferably from 0.98 mole to 1.05 moles, in order to obtain a high molecular weight PAS. An amount less than 0.9 mole or over 1.1 moles is not preferable, since such an amount causes difficulty in producing a PAS with high melt viscosity suitable for working.

The end point of the preliminary polymerization step, that the timing of turning from the preliminary polymerization to the two-phase separated polymerization, is preferably the point when the conversion of the dihalo-aromatic compound has reached 70 mole % to 98 mole %. With a conversion less than 70 mole %, undesirable reactions such as decomposition may occur due to the influence of the

alkali metal sulfide (30 mole % or more). On the contrary, if the conversion exceed 98 mole %, it will be difficult to obtain PAS of a high polymerization degree, even if the two-phase separated polymerization is performed, probably because the polymerization system becomes denatured. A conversion of about 85 mole % to 95 mole % is preferable for obtaining stably a PAS of a high polymerization degree.

Here, the conversion of a dihalo-aromatic compound is calculated according to the formulae shown below.

(a) In the case when a dihalo-aromatic compound (abbreviated DHA) is added in excess of an alkali metal sulfide in terms of molar ratio:

$$\text{Conversion} = \frac{\text{DHA charged (moles)} - \text{Residual DHA (moles)}}{\text{DHA charged (moles)} - \text{Excessive DHA (moles)}} \times 100$$

(b) In other cases than (a):

$$\text{Conversion} = \frac{\text{DHA charged (moles)} - \text{Residual DHA (moles)}}{\text{DHA charged (moles)}} \times 100$$

At the point of turning from the preliminary polymerization to the two-phase separated polymerization, the melt viscosity of the PAS is preferably in the range of from 5 to 300 poise. The range of from 10 poise to 200 poise is more suited for obtaining a PAS of a high polymerization degree with a melt viscosity of 1,000 poise or higher. With a viscosity less than 5 poise, formation of two-phase separation is insufficient, whereby decomposition of the polymerization system or lowering of the reaction rate will readily occur. With a viscosity over 300 poise, harmful substances which will promote polymer cleavage will be accumulated in greater amount, whereby lowering in polymer yield and decomposition of the polymer system will undesirably be caused.

In the two-phase separated polymerization in the process [A] of the present invention, water is preferably added into the preliminary polymerization slurry to control the total water content in the polymerization system to 2.5 moles to 7.0 moles per mole of the alkali metal sulfide charged, the content of water in the solvent being preferably 7 to 30% by weight, thereby causing phase separation into the polymer phase and the solution phase, and the temperature is elevated to 245 to 290°C to carry out polymerization. By the two-phase separated polymerization, a PAS with a melt viscosity of 1,000 poise or higher can be obtained.

If the total water content in the system is less than 2.5 moles, phase separation becomes difficult. On the other hand, if it is over 7.0 moles, the melt viscosity of the PAS formed will be lowered. Particularly, the two-phase separated polymerization is preferably conducted with a total water content ranging from 3.5 moles to 5.0 moles since then a PAS with a high viscosity can easily be obtained. Furthermore, when the polymerization temperature is less than 245°C, only a PAS with low melt viscosity can be obtained. On the other hand, if it exceeds 290°C, there is the possibility of the PAS formed or the polymerization solvent being decomposed. Particularly, the range of from 250°C to 270°C is preferred for producing a PAS with high melt viscosity.

The time required for the two-phase separated polymerization in the process [A] is generally 1 to 50 hours, ordinarily of the order of 1 to 20 hours. If the two-phase separated polymerization time is too short, the condensation polymerization will be insufficient, resulting in only a PAS with low melt viscosity. On the contrary, if it is too long, decomposition may occur. Thus, the polymerization time is preferably from 1 to 15 hours, particularly 3 to 10 hours.

Changing from the preliminary polymerization to the two-phase separated polymerization may be done either by transferring the slurry obtained in the preliminary polymerization to another reaction vessel in which the slurry is subjected to the two-phase separated polymerization conditions or by carrying out the preliminary polymerization and the two-phase separated polymerization by alteration of the polymerization conditions in the same reaction vessel. The time at which water is added may be after polymerization of the preliminary polymerization, preferably before initiation of the temperature elevation to the temperature for the two-phase separated polymerization, in the course of the temperature elevation, or immediately after elevation to the temperature for the two-phase separated polymerization, particularly before initiation of the temperature elevation. Addition of water under the state wherein the amount of the co-existing water is small after it has been maintained for long time at the temperature suitable for the two-phase separated polymerization is undesirable since a PAS with high melt viscosity cannot be obtained.

The solvent to be used in carrying out the two-phase separated polymerization may be the solvent employed in the preliminary polymerization which is the polymerization in the preceding stage, particularly a solvent mixture in which a non-solvent for PAS (particularly high molecular weight PAS), particularly water, is dissolved in an organic amide. This corresponds to the "non-good solvent" as mentioned in the present invention. The "non-good solvent" is described in detail below in the description of the process [B].

In the process [A], the polymerization system is ordinarily maintained under strongly alkaline conditions of pH 9.5 or higher without specific adjustment because a part of alkali sulfide is decomposed and changed into alkali hydroxide with emitting H_2S during dehydration process and therefore it is not specifically required to

adjust the pH. However, when acidic impurities are contained in the starting alkali metal sulfide, it is necessary to make the polymerization system strongly alkaline by addition of at least one member selected from alcoholates, phenolates, hydroxides, oxides and carbonates of alkali metals or the like. The term "strongly alkaline" as herein mentioned means that the pH measure when the reaction mixture is diluted 10-fold with water is in the range of from 9.5 to 14.

Process [B]

The process [B]has more steps than the process [A] and is characterized in that it is more suitable for obtaining an ultra-high molecular weight PAS with a melt viscosity of 7,000 poise or higher than the process[A]. The process [B] comprises cleaning an arylene sulfide prepolymer with a medium to high molecular weight (5 to 3,000 poise, particularly 100 to 2,000 poise) in the cleaning or purifying step and therefore carrying out the liquid-liquid phase separated polymerization as described above, thereby producing an ultra-high molecular weight PAS of 7,000 poise or higher, even some tens of thousands poise or higher in some cases, without the use of a crosslinking agent or an organic carboxylate.

In the process [B], after formation of a medium to high molecular weight, PAS, a semi-solid prepolymer containing a small amount of the solvent is separated from the polymerization system slurry, which prepolymer is washed to remove harmful substances (which may be considered to include certain kinds of organic sulfide compounds and inorganic

sulfur compounds) and then returned again to the poor solvent containing no harmful substances, wherein polymerization is conducted under the liquid-liquid two-phase separated state.

As an alternative for the process B, after cleaning of the PAS of medium to high molecular weight obtained by the preliminary

polymerization, etc., it is dried once to a dry polymer, which is then returned again to a poor solvent containing no harmful substances, wherein polymerization is conducted under two-phase separated state. However, the process [B] is better suited for obtaining easily an ultra-high molecular weight PAS than such an alternative process.

Regardless of whether which process may be employed, preparation of the medium to high molecular weight prepolymer to be subjected to the two-phase separated polymerization step is not limited to the simple preliminary polymerization process as in the process [A]. For, even a PAS prepared by the improved preliminary polymerization in a system in which, for example, $Ca(OH)_2$, CaO, organic carboxylate, etc. are added, will cause no trouble in the two-phase separated polymerization step, because such additives can be removed in the cleaning step.

Additionally the PAS obtained by two-phase separated polymerization can be used in the process [B].

Regardless of whether which process is employed, the prepolymer to be subjected to the two-phase separated polymerization is required to have a melt viscosity (η^*) in the range of from 5 to 3,000 poise, preferably from 100 to 2,000 poise. With a viscosity less than 5 poise or more than 3,000 poise, it is difficult to finally obtain an ultra-high molecular weight PAS.

The amount of the organic amide used is preferably within the range of from 0.2 to 5 liters per mole of the metal sulfide employed in the preliminary polymerization.

The cleaning step of the process [B] is performed specifically as follows. The polymer after completion of the preliminary polymerization is a semi-solid containing a small amount of an organic amide solvent. The semi-solid prepolymer can be separated easily as a wet cake by the filtration method, the decantation method, the centrifugal precipitation method, or another suitable method. When the prepolymer thus separated is in state of a mass or coarse particles, washing internally

of the particles will be insufficient, and therefore it is desirable to crush the prepolymer into fine particles before washing. The washing solution is desirably a strongly alkaline solution of pH 10.0 to 14. The washing solution should also be a non-oxidizable solution, particularly preferably a slightly reductive solution. If the washing solution has a pH less than 10 or is oxidative, the alkali metal sulfide group (-SNa) at the prepolymer terminals may be denatured or decomposed. For the reasons as mentioned above, it is preferable to use as the washing solution an aqueous or alcoholic solution containing at least one of alkali metal sulfides, alkali metal alcoholates, alkali metal phenolates, alkali metal hydroxides, alkali metal oxides and alkali metal carbonates. When the washing solution is attached or remains slightly on the prepolymer, it is desirable to remove amply the washing solution with the same kind of the solvent as that employed in the two-phase separated polymerization (e.g., NMP).

In the two-phase separated polymerization in the process [B], it is desirable that the polymerization system be strongly alkaline (that is, the pH of the 10-fold diluted solution should be within the range of from 9.5 to 14). A pH of less than 9.5 is undesirable since it would give rise to the possibility of substantially no reaction to increase the molecular weight or of decomposition of the polymerization system. For making the polymerization system alkaline, addition of an alkali metal alcoholate, alkali metal phenolate, alkali metal hydroxide, alkali metal oxide, alkali metal carbonate or the like is effective.

The polymerization temperature is within the range of from 245 to 290°C, more preferably from 245 to 270°C.

At a temperature lower than 245°C, prolonged polymerization time is necessary, which is not desirable from the economical point of view. Also, a temperature over 290°C is not preferable, since the polymer may decompose. The time required for polymerization is generally from 1 to 50 hours. With a time shorter than 1 hour, no sufficient increase of the molecular weight can be obtained, while the polymer may decompose if the polymerization time is longer than 50 hours.

The two-phase separated polymerization is carried out by dispersing the cleaned prepolymer which is semi-solid or in dried state obtained in the cleaning step in an appropriate poor solvent and maintaining a specific polymerization temperature with stirring (which is not necessarily required to be a constant temperature).

For the poor solvent to be used in the two-phase separate polymerization, those which can dissolve partially the prepolymer with formation of the high viscosity phase (polymer phase) and the low viscosity phase (solution phase) at the polymerization temperature so that the molecular chains of the prepolymer may move freely to undergo condensation reaction are preferred. Also, a poor solvent having properties which will afford migration of the salt or low molecular weight PAS with certain chain length or lower formed in the polymerization from the polymer phase to the solution phase is preferred. Further, the poor solvent should also satisfy the requirements that it be stable, non-oxidative, neutral or basic at the polymerization temperature. For this solvent, it is preferable to use at least one of organic amides, aromatic hydrocarbons, aliphatic hydrocarbons, ethers, ketones, pyridine, and quinoline derivatives as described in the process [A]. Also, for the solvent, it is desi..ble to use a poor

solvent having a medium dissolving power which will cause phase separation during polymerization. For this purpose, it is preferable to use a non-good solvent decreased slightly in its dissolving power by the addition of 7 to 30 wt.% of water to a good solvent such as an organic amide. The solvent in the two-phase separated polymerization step should be used in an amount of 0.2 to 5 liters per unit of the -(Ar-S)- recurring unit of the PAS charged into the polymerization system.

The post-treatment in the polymerization process of the present invention can be carried out in a conventional manner. For example, after completion of the polymerization reaction of the two-phase separated polymerization, the reaction mixture (in slurry) can be filtered as such without dilution or after dilution with a diluting agent (water, alcohol, hydrocarbon solvent or the like), the polymer being washed with water, dehydrated and dried, thereby to recover an ultra-high molecular weight PAS. When the polymer thus filtered is in state of a mass or coarse particles, it can be pulverized by means of a mixer or the like into fine particles before washing with water, dehydration and drying, to produce a clean ultra-high molecular weight PAS.

The polymer recovered from the slurry of the two-phase separated polymerization may sometimes contain a large amount of alkalis remaining therein, and therefore it is preferable to carry out ample neutralization before washing. If the polymer is dried without neutralization, polyarylenesulfide ion complexes may undesirably be formed.

The polymerization process of the present invention is applicable for not only homopolymerization or random copolymerization but also for block copolymerization. For example, a cleaned p-phenylenesulfide prepolymer and a cleaned m-phenylene prepolymer can be

dispersed in the same polymerization vessel to carry out the two-phase separated polymerization step, whereby a (p-phenylenesulfide)-(m-phenylenesulfide) block copolymer can readily be obtained.

Properties and uses of the PAS formed

From the linear PAS having a large molecular weight thus obtained of the present invention, films and fibers with very great strength and stretchability can be produced. Furthermore, molded products with extremely great impact strength and flexural strength can be obtained. Gel-spinning technique may also be applicable.

The high to ultra-high molecular weight linear PAS of the present invention can also be used as a composition mixed with at least one of synthetic resins such as polyphenylenesulfide copolymer, poly-m-phenylenesulfide, poly-p-phenylenesulfide with low to medium polymerization degree, polyetheretherketone, polyethersulfone, polysulfone, polyimide, polyamide, polyphenyleneether, polyarylene, polycarbonate, polyacetal, liquid crystaline or non-liquid crystalline polyester, fluorine resin, polystyrene, polyolefin and ABS.

Further, the polymer of the present invention can also be used as a composition mixed with at least one of fibrous fillers such as glass fiber, wallastonite, potassium titanate fiber, ceramic fiber, and asbestos, and powdery fillers such as mica, silica powder, alumina powder, titanium oxide powder, calcium carbonate powder, talc, clay, and glass powder.

EXPERIMENTAL EXAMPLES

Example A1

(1) Preliminary polymerization:

A 20-liter Ti-lined autoclave was charged with 11.0 Kg of N-methyl-2-pyrrolidone (hereinafter abbreviated NMP) and 4.239 Kg (25.0 moles as Na_2S) of $Na_2S \cdot 5H_2O$ crystals containing 46.02 wt.% of Na_2S (produced by Nagao Soda K.K.), and the temperature was

elevated gradually with stirring in a nitrogen atmosphere over about 2 hours up to 203°C to distill off 1.585 Kg of water, 1.96 Kg of NMP, and 0.58 mole of H_2S. In this case, the content of water in the system was changed to about 1.6 moles per mole of Na_2S.

After the mixture was cooled to 130°C, 3.59 Kg (24.42 moles) of p-dichlorobenzene (hereinafter abbreviated p-DCB) and 3.17 Kg of NMP were added, and polymerization was carried out at 210°C for 10 hours to obtain a preliminary polymerization slurry (S - 1).

The residual p-DCB content in the slurry was determined by gas chromatography, from which the conversion of p-DCB was determined according to the above formula (b) for calculation of conversion. The conversion was found to be 95.0 mole %.

100 g of the slurry was taken out and subjected as it was to filtration by aspiration to remove liquid components. Then the solid was dispersed in about 1 Kg of deionized water and again subjected to filtration by aspiration for washing of the PPS produced. After this operation was repeated three times, the washed product was dried at 100°C for 2 hours (in air atmosphere) to obtain polyphenylenesulfide (PPS) powder. A press sheet was obtained by melt pressing of the powder without pre-heating at 320°C for 30 seconds. The melt viscosity of this sheet was measured by the use of a Kōka type flow tester (produced by Shimazu Seisakusho K.K.) at 310°C (preheating: 5 minutes). The viscosity as calculated on the basis of a shearing rate of 200 $(sec.)^{-1}$ was 1C5 poise.

(2) Two-phase separated polymerization:

Into a one-liter autoclave was charged 754 g of the slurry (S - 1) (corresponding to one mole of Na_2S charged). 52.2 g of water (4.5 mole/1 mole Na_2S as the total water content) was added thereto, and polymerization was carried out at a temperature elevated

to 250°C in a nitrogen atmosphere for 10 hours. The conversion of p-DCB was found to be 99.0%. After cooling, pearl-like PPS were separated by screening through a screen with a mesh size of about 0.1 mm. A portion of the slurry before screening was diluted 10-fold with water, and its pH was measured to be 10.9. Then the product was neutralized with dilute hydrochloric acid, washed repeatedly with deionized water, and dried at 100°C for 3 hours to obtain a PPS. The yield was found to be about 84%.

The pearl-like PPS thus obtained had an apparent specific gravity of 43 g/dl and a melt viscosity of 5,000 poise.

Examples A2 - A8

By the use of the slurry of S - 1, two-phase separated polymerizations were carried out according to the procedure in Example 1A by varying the polymerization time within the range from 1 to 15 hours (Examples A2 - A5). Also, by the use of the slurry of S - 1, two-phase separated polymerizations were carried out by varying the water content added to the co-existing water content in terms of H_2O/Na_2S molar ratio of 3.0 to 5.0 (Examples A6 - A8). In every case, a pearl-like PPS with high melt viscosity was obtained. The results are summarized in Table 2.

Examples A9 - A19

According to substantially the same procedure as in the preliminary polymerization as in Example A1, various slurries (S-2-7, S-10-14) were obtained by varying the molar ratio (p-DCB/Na_2S molar ratio), the co-existing water content (H_2O/Na_2S molar ratio), the concentration charged (moles of Na_2S in 1 Kg of NMP), the polymerization temperature, and the polymerization time. For each polymer, the conversion and the melt viscosity of the PPS formed were determined. the polymerization condition and the results are as shown in Table 1.

By the use of these slurries, two-phase separated

polymerizations were conducted under various conditions as shown in Table 2. The results were as shown in Table 2.

Comparative Example A1

Into a one-liter autoclave was charged 754 g of the preliminary polymerization slurry (S - 1), and, without addition of water, two-phase separated polymerization was carried out in a nitrogen atmosphere at 250°C for 10 hours.

After cooling, PPS was separated from NMP by aspirating filtration. Then the PPS was neutralized with dilute hydrochloric acid, repeatedly washed with deionized water, and dried at 100°C for 5 hours to obtain a fine powder polymer. The yield was 98%, the melt viscosity being 80 poise and the apparent specific gravity 12 g/dl. The results are summarized in Table 2.

Comparative Example A2

Following substantially the same procedure as in Example A1 except for changing the amount of coexisting water to 2.5 moles per mole of Na_2S, polymerization was carried out at 210°C for 10 hours to obtain a preliminary polymerization slurry (S - 8). The conversion was 89.8%, and the melt viscosity of the PPS formed was 5 poise or less. The results are summarized in Table 1.

This slurry (770 g) was charged into a one-liter autoclave and, with addition of 36 g of water, two-phase separated polymerization was conducted in a nitrogen atmosphere at 250°C for 10 hours to obtain a granular PPS. The yield was 78%, and the melt viscosity of the PPS was 430 poise. When the water content in the preliminary phase polymerization was excessive, melt viscosity could not become high, and the slurry after two-phase separated polymerization tended to decompose with generation of bad odor. The results are summarized in Table 2.

Comparative Example A3

Into a 20-liter autoclave, 12.0 Kg of NMP, 4.07 Kg (24.0 mole as Na_2S) of $Na_2S.5H_2O$ crystals containing 46.0 wt. % of Na_2S and 3.705 Kg (25.20 moles) of p-DCB were charged and, without withdrawl of water, the reaction was carried out in a nitrogen atmosphere at 210°C for 20 hours to obtain a preliminary polymerization slurry (S -9). The conversion was 83.0%, and the melt viscosity of the PPS obtained by the preliminiary polymerization was 5 poise or less. The results are summarized in Table 1.

The slurry (S - 9) (824 g) was charged into a one-liter autoclave, and two-phase separated polymerization was carried out in a nitrogen atmosphere at 250°C for 10 hours. As a result, decomposition occurred without progress of polymerization. The granular PPS obtained in a small amount had a melt viscosity of 20 poise or less. The results are summarized in Table 2.

Comparative Example A4

The preliminary polymerization slurry obtained in Comparative Example A3 (S - 9) (824 g) was charged into a one-liter autoclave and, without addition of water, polymerization was further carried out in a nitrogen atmosphere at 210°C for 30 hours, thus carrying out polymerization in the presence of about 5.1 moles of co-existing water per one mole of Na_2S for a total period of 50 hours. As a result, the reaction mixture was found to have decomposed with generation of bad odor. The PPS recovered in a small amount had a melt viscosity of 20 poise or less.

Comparative Example A5

Into a one-liter autoclave was charged 898 g of the slurry (S - 5) (corresponding to 1.2 moles of Na_2S charged), and polymerization was carried out at a temperature elevated to

IA

250°C in a nitrogen atmosphere for 5 hours to complete the reaction. After cooling, 150 g of the slurry was sampled, and the conversion was determined following the formula (a) for calculation of conversion. Melt viscosity of the PPS formed was also determined.

Conversion: 99.2 mole %

Melt viscosity of PPS: 82 poise

Then, 57.6 g of water was added to the remaining slurry (4.5 mols. as the total amount), and the temperature was elevated again to 250°C, which the reaction was carried out for 10 hours to produce a sandy or granular PPS. The yield was 68%, the apparent specific gravity being 31 g/dl and the melt viscosity 900 poise.

If the conversion is too great in the preliminary polymerization, the melt viscosity will not be increased even though two-phase separated polymerization may be conducted under the conditions of the present invention.

Example A20

A 10-liter autoclave was charged with 4,500 g of NMP and 1,696 g (10 moles as Na_2S) of $Na_2S \cdot 5H_2O$ crystals containing 46.02 wt. % of Na_2S, and the temperature was elevated gradually with stirring in a nitrogen atmosphere up to 202°C to distill off 683 g of water, 417 g of NMP, and 0.31 mole of H_2S. In this case, the content of water in the system was changed to about 1.33 moles per mole of Na_2S. After the mixture was cooled to 130°C, 1439 g of p-DCB (p-DCB/Na_2S molar ratio 1.01/1.00) and 762 g of NMP were added, and polymerization was carried out at 210°C for 10 hours to obtain a preliminary polymerization slurry. A small amount of this slurry was sampled for examination. The conversion was found to be 93.5%, and the melt viscosity of the PPS formed was about 100 poise.

Next, without cooling the preliminary polymerization slurry, 466 g of water was pressurized thereinto with nitrogen (to a total water content of

4.0 moles per mole of Na_2S), and the temperature of the mixture was elevated to 260°C, which two-phase separated polymerization was carried out for 10 hours. The conversion of p-DCB was 99.4%. Subsequently, by the same procedure as in Example 1A, pearl-like PPS was recovered. The polymer yield was 86%, and the melt viscosity 7,400 poise.

Comparative Example A6

A one-liter autoclave was charged with 754 g of the homogeneous solution polymerization slurry (S - 1) and, without addition of water (total water content of 1.6 moles per mole of Na_2S), polymerization was carried out in a nitrogen atmosphere at a temperature elevated to 250°C to complete the reaction. Then, without cooling of the mixture, 52.2 g of water was pressurized thereinto with nitrogen gas. The temperature was once lowered to about 220°C, and the mixture was heated again to 250°C, whereupon heating was immediately discontinued. Recovery of the polymer according to the same procedure as in Example 1 produced a granular (non-spherical) PPS. The conversion of p-DCB was 99.3%, the yield being 70% and the melt viscosity of PPS 260 poise.

Comparative Example A7

A one-liter autoclave was charged with 754 g of a slurry (S - 1) obtained by polymerization at 210°C for 10 hours under the condition of a content of 1.6 moles of H_2O per mole of Na_2S, and, with addition of 52.2 g of water (4.5 moles of total water content per mole of Na_2S), the temperature was elevated in a nitrogen atmosphere from room temperature to 250°C over about one hour. On reaching 250°C, the mixture was immediately cooled. The conversion of p-DCB was found to be 95.8%. Subsequently, the same post-treatment as in Example A1 was conducted. A granular (non-spherical) PPS was obtained. The polymer yield was about 68%, and the melt viscosity was 400 poise.

Example A21

Homogeneous solution polymerization was carried out under exactly the same conditions as in Example A1, and this step was followed by two-phase separated polymerization at 250°C for 10 hours. Next, after the mixture had been maintained at 250°C for 30 minutes while stopping stirring, the mixture was cooled to room temperature over about 2 hours with the stirring being stopped. Following subsequently the same post-treatment as in Example A1, substantially pearl-like PPS was obtained. The yield was 83%, and the melt viscosity 5,400 poise.

The particle size distribution was found to be approximately the same as in Example A1, without flattening or fusion of individual particles. Thus, pearl-like particles are not formed in the course of cooling after two-phase separated polymerization, but they are considered to be formed during the two-phase separated polymerization and hardened thereafter gradually to the extent which will not cause fusion of the particles.

Table 1. Homogeneous solution polymerization slurry

Slurry	Polymerization Conditions					Conversion of preliminary polymerization (mole%)	Viscosity melt of polymer formed (poise)	Remarks
	Concentration charged (Na_2S mole/KgNMP)	Monomer ratio (p-DCB/Na_2S molar ratio)	Co-existing water amount (H_2O/Na_2S molar ratio)	Polymerization temperature (°C)	Polymerization time (hours)			
S-1	2.00	1.00	1.6	210	10	95.0	105	Example
2	"	"	"	"	5	90.8	50	"
3	"	"	"	"	20	96.7	250	"
4	"	"	1.1	"	10	95.6	125	"
5	"	1.02	1.3	"	10	96.0	94	"
6	"	1.00	1.4	"	10	95.7	84	"
7	"	"	2.0	"	10	95.1	45	"
8	"	"	2.5	"	10	89.8	<5	Comp. Example
9	"	1.05	5.1	"	20	83.0	<5	"
10	"	1.00	1.4	"	1	56.4	6	Example
11	"	"	"	"	3	77.3	6	"
12	"	1.01	1.5	220	5	92.4	45	"
13	"	"	"	230	5	94.5	35	"
14	2.50	1.01	1.4	210	10	93.2	40	"

Table 2. Two-phase separated polymerization results

No.	Polymerization Conditions						Conversion	Yield	Melt viscosity	Remarks
	Two-phase separated polymerization slurry	p-DCB/Na_2S molar ratio	Co-existing water amount (H_2O/Na_2S molar ratio)	(*) pH	Polymerization temperature (°C)	Polymerization time (hours)	(%)	(%)	(poise)	
Exam. A1	S-1	1.00	4.5	10.9	250	10	99.0	84	5000	
A2	"	"	"	9.8	"	1	97.4	72	1300	
A3	"	"	"	10.0	"	3	98.6	74	2100	
A4	"	"	"	10.3	"	5	98.6	79	3060	
A5	"	"	"	11.0	"	15	99.3	82	4800	
Comp. Exam. A1	"	"	1.6	9.3	"	10	99.6	98	80	
Exam. A6	"	"	3.0	11.2	"	"	98.9	78	3200	
A7	"	"	4.0	10.8	"	"	98.9	83	4500	
A8	"	"	5.0	10.9	"	"	99.1	85	3400	
Exam. A9	S-2	"	4.5	9.9	250	10	98.7	79	3300	
A10	S-3	"	"	10.7	"	"	99.5	79	3800	
A11	S-4	"	"	11.0	"	"	99.0	83	5000	
A12	S-5	1.02	"	10.2	"	"	99.2	86	3500	
A13	S-6	1.00	"	11.2	"	"	98.9	82	7000	
A14	S-7	"	"	11.0	"	"	98.9	83	5600	

Table 2. (Continued)

No.	Polymerization Conditions						Conversion	Yield	Melt viscosity	Remarks
	Two-phase separated polymerization slurry	p-DCB/Na_2S molar ratio	Co-existing water amount (H_2O/Na_2S molar ratio	(*) pH	Polymerization temperature (°C)	Polymerization time (hours)	(%)	(%)	(poise)	
Comp. Exam. A2	S-8	1.00	4.5	7.4	250	10	98.5	78	430	
A3	S-9	1.05	5.1	6.9	"	"	98.8	-	<20	
Exam. A15	S-10	1.00	4.5	9.7	"	"	98.4	69	1800	Slightly tending to decompose
A16	S-11	"	"	9.8	"	"	98.6	81	2100	Slightly tending to decompose
A17	S-12	1.01	4.5	11.2	260	10	99.3	86	6000	
A18	S-13	1.01	4.5	11.2	260	10	99.3	85	5200	
A19	S-14	1.01	4.0	10.9	255	10	99.2	87	3000	

(*) Value measured for the slurry after the reaction diluted 10-fold with water.

Example B1

(1) Preliminary polymerization step:

A Ti-lined 20-liter autoclave was charged with 11.0 Kg of NMP and 25.0 moles of $Na_2S \cdot 5H_2O$, and the residual water content in the vessel was controlled to 1.5 moles per mole of Na_2S charged by distilling off water and a slight amount of NMP while elevating the temperature of the mixture up to about 200°C. During this operation, 0.59 mole of H_2S was also distilled off. With addition of 24.41 moles of p-dichlorobenzene and 3.15 Kg of NMP to the mixture, polymerization was carried out at 212°C for 7 hours to obtain a polymerized slurry. The polymer in the slurry was found to have a η^* of 120 poise.

To the polymerized slurry were added 75 moles of water (total water content 4.5 moles/mole of Na_2S charged), and two-phase separated polymerization was carried out at 260°C for one hour to obtain a prepolymer slurry (S-B1). The polymer in the (S-B1) was found to have a η^* of 610 poise.

(2) Cleaning step-two-phase separated polymerization step:

By filtration of 1,000 g of the slurry (S-B_1), the liquid phase was separated to obtain a solid, which was washed with an aqueous solution of Na_2S with pH 12.8 (Na_2S = 1 wt.%) to obtain a coarse particulate prepolymer. This polymer was crushed with a mixer into coarse particles of about 2 mm or smaller, again washed with the aqueous Na_2S solution with pH 12.8, and then washed twice with NMP to remove adherent water to obtain a wet cake of the cleaned polymer. (Completion of the cleaning step)

The wet cake was transferred into a one-liter autoclave and, with addition of 550 ml of NMP containing 12.5 wt.% of water, heated at 255°C for 4 hours to carry out two-phase separated polymerization (pH of 10-fold diluted slurry = 10.1). After completion

of the reaction, the particulate polymer was filtered from the polymerized slurry, crushed with a mixer into particles of 2 mm or smaller, neutralized with dilute hydrochloric acid, washed with water, dehydrated and dried to produce the final polymer. This polymer was found to have a η^* of 14,500 poise.

Example B2

The steps of cleaning and two-phase separated polymerization (pH after 10-fold dilution of slurry = 10.2) were practiced according to the procedures in Example B1 except for carrying out cleaning of the polymer in the slurry (S-B1) of Example B1 with an aqueous solution with pH = 13.2 (Na_2S 2.3%) and carrying out two-phase separated polymerization at 260°C for 4 hours to obtain a final polymer. This polymer was found to have a η^* of 18,000 poise.

Example B3

The steps of cleaning and two-phase separated polymerization (pH after 10-fold dilution of slurry = 9.9) was practiced according to the procedures in Example B1 except for carrying out two-phase separated polymerization by the use of the polymer in the slurry (S-B1) of Example B1 and 600 ml of a solvent mixture of NMP containing 9.5 wt.% of water/isopropylnaphthalene = 85/15 (weight ratio) to obtain a final polymer. This polymer was found to have a η^* of 10,500 poise.

Example B4

The polymer in the slurry (S-B1) of Example B1 was employed. Except for carrying out washing in the cleaning step with an aqueous Na_2S solution with pH 13.2 and carrying out two-phase separated polymerization at 255°C for 15 hours, the procedures of the cleaning step and the two-phase separated polymerization step (pH after 10-fold dilution of slurry = 10.1) as in Example B1 were repeated to obtain a final polymer. This polymer was found to have a η^* of 10,100 poise.

Example B5

(1) Preliminary polymerization step:

A one-liter autoclave was charged with 550 g of NMP and 1.25 mole of $Na_2S \cdot 5H_2O$, and water and a small amount of NMP were distilled off while the temperature was elevated to about 200°C to control the residual water content in the vessel to 1.5 mole per mole of Na_2S charged. During this operation, 0.03 mole of H_2S was also distilled off.

1.22 Mole of p-dichlorobenzene and 160 g of NMP were added to the mixture, and preliminary polymerization was carried out at 220°C for 4 hours to obtain a polymerized slurry. The polymer formed in this slurry was found to have a η^* of 95 poise.

To the slurry was added 3.75 moles of water (total water content =4.5 moles/mole of Na_2S charged) and two-phase separated polymerization was carried out at a temperature of 260°C for 2.0 hours to obtain a prepolymer slurry (S-B2). The polymer formed in this slurry (S-B2) was found to have a η^* of 1,900 poise.

(2) Cleaning and two-phase separated polymerization:

The cleaning step and the two-phase separated polymerization step of Example B1 were repeated except for the use of the polymer in (S-B2) obtained in the step (1) and NMP containing 20 wt. % of water as the solvent in the two-phase separated polymerization step to obtain a final polymer (pH of slurry diluted to 10-fold = 9.8). This polymer was found to have a η^* of 12,000 poise.

Comparative Example B1

The polymer in the slurry (S-B1) of Example B1 was employed. The cleaning and two-phase separated polymerization steps were practiced according to the procedures in Example B2 except for the use of an aqueous sodium peroxide solution with pH 13.2 in place of the aqueous Na_2S solution with pH 13.2 in the cleaning step. The polymer was completely decomposed,

and recovery of the final polymer was impossible.

Comparative Example B2

The polymer in the slurry (S-B1) of Example B1 (η^* = 610 poise) was employed. The cleaning and the two-phase separated polymerization steps (pH of slurry diluted to 10-fold = 8) were practiced according to the procedures in Example B1 except for using NMP containing 60 wt.% of water as the solvent in the two-phase separated polymerization step to obtain a final polymer. The polymer was found to have a η^* of 690 poise, indicating substantially no increase in viscosity.

Example B6

A 10-liter Ti-lined autoclave equipped with stirring blades was charged with 70 liters of NMP, and 7.5 moles of $Na_2S \cdot 3H_2O$ and 15.0 moles of CaO were added into the autoclave, which was then sealed. After replacement with N_2, under stirring, dehydrating reaction with CaO was carried out by heating the mixture at 160°C for one hour. Then a mixture of 0.5 liter of NMP and 7.5 moles of p-DCB was added, and polymerization was conducted for 5.0 hours, while the inner temperature in the autoclave was controlled at 200°C. After the reaction, solids were separated from the reaction mixture, neutralized with dil. HCl, thoroughly washed with water until the pH of washing became approximately 7.0, dehydrated, and dried in vacuo at 80°C to obtain a prepolymer. The fine powdery prepolymer was found to have a melt viscosity of 590 poise.

The fine powdery prepolymer (54.0 g) was charged into a one-liter Ti-lined autoclave, and 600 g of NMP, 97 g of water, and 2.0 g of C_2H_5ONa were added thereto. The temperature was then elevated to 260°C, at which two-phase separated polymerization was conducted for 4 hours. The polymerized slurry (pH of slurry diluted 10-fold with water = 11.5) was screened, and the polymer thus obtained was thoroughly neutralized with dil. HCl, washed with water, and dried in vacuo at 80°C to

obtain a final polymer. This polymer was found to have a melt viscosity of 39,000 poise.

Comparative Example B3

Two-phase separated polymerization was carried out under the conditions set forth in Example B6 except for omission of addition of C_2H_5ONa. The slurry obtained was found to have a decomposition odor, the pH of the slurry diluted 10-fold with water being 7.3. The final polymer obtained had a η^* value of only 20 poise.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for producing a high molecular weight to ultra-high molecular weight linear polyarylenesulfide, which comprises carrying out a two-phase separated polymerization comprising dissolving an arylenesulfide prepolymer having a melt viscosity of 5 to 3,000 poise (at 310°C, shearing rate = 200 $(sec.)^{-1}$) in a poor solvent under a strongly alkaline condition (in a pH range of from 9.5 to 14 of the reaction mixture when diluted 10-fold with water) in a temperature range of from 245°C to 290°C into a liquid-liquid two-phase separated state and maintaining said state for 1 to 50 hours to convert the arylenesulfide prepolymer into a high molecular weight polymer, then separating the polymer from the polymerization system, and purifying the polymer after neutralization.

2. A process according to Claim 1, wherein the poor solvent in the two-phase separated polymerization is a solvent mixture comprising an organic amide and 7 to 30 wt.% of water.

3. A process according to Claim 1, wherein the arylenesulfide is at least one member selected from the group consisting of p-arylenesulfides and m-arylenesulfides.

4. A process according to Claim 1, wherein the pH is adjusted for the two-phase separated polymerization by the addition of an alcoholate, phenolate, hydroxide, oxide or carbonate of an alkali metal.

5. A process according to Claim 1, wherein said arylenesulfide prepolymer is prepared by a preliminary polymerization, comprising carrying out polymerization reaction by heating an alkali metal sulfide and a dihalo-aromatic compound in an organic amide

containing 0.5 to 2.4 moles of water per mole of the alkali metal sulfide charged in a temperature range of from 180°C to 240°C under a preliminary polymerization state until the conversion of the dihalo-aromatic compound becomes 70 to 98 mole %; the residual alkali metal sulfide content becomes 30 mole % or less; and the melt viscosity of the polymer produced has a melt viscosity of 5 to 3,000 poise, and thereafter adding additional water into the polymerization system to a water content of 2.5 to 7.0 moles per mole of the alkali metal sulfide charged, and said two-phase separated polymerization is practiced by elevating the polymerization system to a temperature in the range of from 245°C to 290°C while maintaining the system under a strongly alkaline condition to dissolve the prepolymer into a liquid-liquid two-phase separated state, which state is maintained for 1 to 50 hours, thereby converting the arylenesulfide prepolymer into a high molecular weight polymer.

6. A process according to Claim 5, wherein the dihalo-aromatic compound comprises at least one memuer selected from p-dihalobenzenes and m-dihalobenzenes.

7. A process according to Claim 5, wherein the pH is adjusted to the strongly alkaline condition in the two-phase separated polymerization by addition of an alcoholate, phenolate, hydroxide, oxide or carbonate of an alkali metal.

8. The process according to Claim 1, wherein said prepolymer is a wet product of a polyarylenesulfide having a melt viscosity of 5 to 3,000 poise which has been produced by the reaction of an alkali metal sulfide and a dihalo-aromatic compound in a solvent, follwed by separating the polymer thus produced, and washing the polymer with a non-oxidative alkali solution.

9. A process according to Claim 8, wherein said arylenesulfide prepolymer is a polyarylenesulfide having a melt viscosity of 5 to 3,000 poise which is in the form of dried powder substantially cleaned.

10. A process according to Claim 8, wherein the non-oxidative alkaline solution in the step of cleaning the prepolymer is an aqueous solution with a pH of 10 to 14 containing a sulfide, alcoholate, phenolate, hydroxide, oxide or carbonate of an alkali metal.

11. An ultra-high linear polyarylenesulfide having a melt viscosity of 7,000 poise or higher, produced by the process of Claim 1.

12. The process according to Claim 1, wherein said prepolymer is a wet product obtained by reacting an alkali metal sulfide with a dihalo-aromatic compound in an organic amide containing a lower quantity of water per mole of the alkali metal sulfide charged, at a temperature of 160°C to 260°C, until an arylenesulfide polymer having a melt viscosity of 5 to 3,000 poise determined at 310°C and a shear rate of 200 sec^{-1} is formed, separating the polymer, and washing the polymer with a non-oxidative alkali solution.

13. The process according to Claim 1, wherein said prepolymer is a wet product obtained by reacting an alkali metal sulfide with a dihalo-aromatic compound in an organic amide containing a lower quantity of water per mole of the alkali metal sulfide charged, at a temperature of 160°C to 260°C, heating the thus obtained polymer at a temperature of from 245°C to 290°C in a solvent of a strongly alkaline mixture of an organic amide and 7 to 30% by weight of water until an arylenesulfide polymer

having a melt viscosity of 5 to 3,000 poise determined at 310°C and a shear rate of 200 sec^{-1} is formed separating the polymer, and washing the polymer with a non-oxidative alkali solution.

14. A process for producing a high to ultra-high molecular weight linear polyarylene sulfide which comprises subjecting an arylene sulfide prepolymer, having a melt viscosity of 5 to 3,000 poise measured at 310°C and a shear rate of 200 sec^{-1}, to a liquid-liquid two-phase separated polymerization under strongly alkaline conditions at a temperature of about 245°C to 290°C.

15. The process of Claim 14, wherein said two-phase polymerization is carried out in a poor solvent for said prepolymer.

16. The process of Claim 15, wherein said poor solvent is an organic amide containing about 7 to 30% by weight water.

17. A process for producing high to ultra-high molecular weight linear polyarylene sulfide which comprises forming an arylene sulfide prepolymer and further polymerizing said prepolymer under strongly alkaline conditions at a temperature of about 245°C to 290°C in a liquid-liquid two-phase separated polymerization.

18. The process of Claim 17, wherein said prepolymer is formed in an organic amide solvent, followed by addition of a phase separating agent to form two liquid phases consisting of a polymer solution phase and a solvent phase.

19. The process of Claim 18, wherein said phase separating agent is a poor solvent for said arylene sulfide prepolymer.

20. The process of Claim 19, wherein said poor solvent is water.

21. The process of Claim 20, wherein the quantity of water added is sufficient to raise the water content to about 7 to 30% by weight of the organic amide solvent.

22. The process of Claim 21, wherein said organic amide solvent is N-methylpyrrolidone.

23. The process of Claim 22, wherein said prepolymer has a melt viscosity of 5 to 300 poise measured at 310°C and shear rate of 200 sec^{-1}.

24. The process of Claim 17, wherein said prepolymer is washed prior to further polymerizing.

25. The process of Claim 24, wherein said washed prepolymer is dispersed in a poor solvent which forms two liquid phases consisting of a polymer solution phase and a solvent phase.

26. The process of Claim 25, wherein said poor solvent is an organic amide solvent containing about 7 to 30% by weight water.

27. The process of Claim 26, wherein said prepolymer is washed with a non-oxidative alkali solution.

28. The process of Claim 27, wherein said organic amide solvent is N-methylpyrrolidone.

29. The process of Claim 28, wherein said prepolymer has a melt viscosity of 100 to 2,000 poise measured at 310°C and shear rate of 200 sec^{-1}.

FETHERSTONHAUGH & CO.
OTTAWA, CANADA

PATENT AGENTS